

## CPP 48: Nanoparticles and Composite Materials II

Time: Friday 10:30–13:00

Location: ZEU 114

CPP 48.1 Fri 10:30 ZEU 114

**Random nanoparticle patterns as unique optical labels for secure identification** — ●ALEXANDER SCHWEMER<sup>1</sup>, ULRICH RÜHRMAIR<sup>2</sup>, and ULRICH RANT<sup>1</sup> — <sup>1</sup>Walter Schottky Institut, Technische Universität München, Am Coulombwall 3, 85748 Garching — <sup>2</sup>Institut für Informatik VI, Technische Universität München, Boltzmannstraße 3, 85748 Garching

Complex macro-structures consisting of nanoscale objects hold great potential to be used as unique labels for secure identification, because the nanoscale features render it impossible to re-produce, i.e. forge, these patterns with nm accuracy on a large scale. Here, we present a straightforward and inexpensive approach to create and read-out optical labels based on ensembles of individual metallic nanoparticles. Gold nanorods, which exhibit two plasmonic resonances with distinct spectral and polarization features, are sparsely dispersed and immobilized on a solid substrate. Light scattered from the individual particles is imaged by a dark-field microscopy setup onto a consumer-electronics grade RGB CCD camera. By recording a set of polarization dependent images we are able to deduce a specific set of parameters for each particle which encompasses the particle's position (accuracy 150 nm), its spectral properties (color), and its angular orientation on the substrate (accuracy 0.2°). We describe the experimental realization and data-analysis routines to extract an extensive set of unique data in parallel from the nano-pattern and outline the implications of the introduced concept for future use in highly sensitive security applications for valuable items such as bank notes, passports or commercial goods.

CPP 48.2 Fri 10:45 ZEU 114

**New approach to low-temperature processed titania for application in inorganic-organic hybrid photovoltaics** — ●MONIKA RAWOLLE<sup>1</sup>, MATTHIAS A. RUDERER<sup>1</sup>, SHUAI GUO<sup>1</sup>, EZZELDIN METWALLI<sup>1</sup>, ERIK V. BRADEN<sup>1</sup>, JAN PERLICH<sup>2</sup>, STEPHAN V. ROTH<sup>2</sup>, THOMAS FRÖSCHL<sup>3</sup>, NICOLA HÜSING<sup>3</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik Department, LS Funkt. Mat., James-Franck-Str. 1, 85748 Garching, Germany — <sup>2</sup>HASYLAB at DESY, 22603 Hamburg, Germany — <sup>3</sup>Universität Salzburg, Materialforschung und Physik, Salzburg, Austria

Crystalline titania is a widely researched inorganic semiconductor for inorganic-organic hybrid photovoltaics. Among its many advantages are low cost and easy producibility, with the disadvantage of a necessary high-temperature step to obtain the crystalline anatase or rutile polymorph. A possible precursor for titania which does not require a high-temperature step to obtain crystallinity was previously used to create crystalline titania particles with the inverse microemulsion technique for usage in catalysis. [1] We use this precursor to prepare thin films on flexible substrates. The structure is controlled with the diblock copolymer poly(styrene-block-ethylene oxide) [P(S-b-EO)] as templating agent in a so-called good-poor solvent pair induced microphase separation combined with sol-gel chemistry. The structure of the titania films is investigated with XRR and GISAXS. Crystallinity is determined with GIWAXS for different temperatures and related to optical properties as probed with UV/Vis spectroscopy.

[1] R. Rossmannith et al., Chem. Mater. (2008) 20, 5768-5780

CPP 48.3 Fri 11:00 ZEU 114

**Geordnete Nanopartikel zur Erzeugung von Höheren Harmonischen** — ●VALERIE MONDES<sup>1</sup>, CHRISTINA GRAF<sup>1</sup>, JÜRGEN PLENGE<sup>1</sup>, QI GAO<sup>1</sup>, MATTHIAS BUCHHOLZ<sup>1</sup>, MATTHIAS KLING<sup>2</sup> und ECKART RÜHL<sup>1</sup> — <sup>1</sup>Freie Universität Berlin, Physikalische und Theoretische Chemie, Takustr. 3, 14195 Berlin — <sup>2</sup>MPQ, Hans-Kopfermann-Str. 1, 85748 Garching

Neuartige Methoden zur Erzeugung Höherer Harmonischer nutzen die lokale Feldverstärkung in geordneten nanoskopischen Strukturen, indem die resonante Anregung von Plasmonen zur Feldverstärkung in Gegenwart von Edelgasen erfolgt. Es wird in dieser Arbeit die Bildung von geordneten Arrays von Nanopartikeln zur Erzeugung von kurzwelliger Strahlung genutzt. Sie bestehen aus geordneten Strukturen von isotropen und anisotropen Goldnanopartikeln, da von ihnen ausgeprägte nanoplasmonische Eigenschaften erwartet werden. Die Nanopartikel werden mit unterschiedlicher Form und Größe mit Methoden der Kolloidchemie hergestellt und durch induzierte Selbstorganisation

auf Saphirträgern in Monolagen angeordnet. Die erzeugten, geordneten Nanostrukturen können damit Dimensionen bis hin zu Quadratzentimetern erreichen. Dies ist von Bedeutung, wenn durch Laserstrahlung die Strukturen beschädigt werden und stets unbeschädigte Nanostrukturen zur Erzeugung Höherer Harmonischer genutzt werden sollen. Es wurde ein Aufbau zur Detektion von kohärenten ultrakurzen XUV-Pulsen mittels eines XUV-Monochromators aufgebaut und charakterisiert. Es wird über Arbeiten zur Emission von kurzwelliger Strahlung aus den Nanostrukturen berichtet.

CPP 48.4 Fri 11:15 ZEU 114

**Light induced electron spin resonance studies on films for hybrid solar cells** — ●FLORIAN WITT, MARTA KRUSZYNSKA, IRINA LOKTEVA, NIKOLAY RADYCHEV, JOANNA KOLNY-OLESIK, HOLGER BORCHERT, and JÜRGEN PARISI — University of Oldenburg, Department of Physics, Energy and Semiconductor Research Laboratory (EHF), 26111 Oldenburg, Germany

Light induced electron spin resonance spectroscopy (l-ESR) is a widely used tool for the investigation of long living charges in conjugated polymers as well as in blends for organic and hybrid photovoltaics. Latter one is a synonym for solar cells out of a blend of colloidal prepared, inorganic nanocrystals and an organic conjugated polymer which act as a donor/acceptor system. With l-ESR two limiting factors in hybrid blends were investigated. At first we show the influence of traps related to unpassivated surface states on the charge carrier recombination. These states occur due to the necessary ligand exchange of the nanoparticles (A thick ligand shell resulting from colloidal synthesis needs to be replaced by smaller molecules such as pyridine to enable charge transfer). The influence of the ligand exchange treatment on the charge carrier recombination will be shown. A second focus lies on so called charge transfer complexes (CTC) in hybrid blends. These states consist of a bound polaron pair at the donor acceptor interface. We show their occurrence by l-ESR.

CPP 48.5 Fri 11:30 ZEU 114

**Blinking and spectral diffusion of single CdSe/ZnS colloidal nanoparticles** — ●DANIEL BRAAM, MATTHIAS OFFER, GÜNTHER PRINZ, MARTIN GELLER, and AXEL LORKE — Fakultät für Physik und CeNIDE, Universität Duisburg-Essen, 47048 Duisburg

Even though nanoparticles have been a main interest in research for decades, their luminescent behaviour still holds many secrets to disclose. The power-law of on- and off-times of random emission intermittency as well as several shifts in the emission wavelength still lack of a unified theory [1]. We investigated the excitonic structure of CdSe/ZnS core/shell nanoparticles using a micro-photoluminescence ( $\mu$ -PL) setup with a 405 nm cw-laser. To ensure single-particle-PL we dispersed the nanoparticles in toluene with 1% PMMA and deposited these dilute solution through spin-coating on different substrates. We observed substrate-dependent emission intermittency up to nearly blinking-free emission, which we can attribute to a single CdSe nanoparticle. Spectral jumps of 25 meV in the emission can be assigned to excitonic transitions altered by a charged nanoparticle or an outer charged electronic trap state [2]. Furthermore, we observed a phonon replica of 25 meV and smaller (<10 meV) energetic shifts of the emission lines which are likely due to random charge variation in the surrounding of the nanoparticle.

[1] P. Frantsuzov et al., Nature 4, 519 (2008).

[2] A. Efros, Nature Mat. 7, 612 (2008).

CPP 48.6 Fri 11:45 ZEU 114

**New Approach to Photoluminescence Intermittency: Luminescence Intensity-resolved Investigation of CdSe/ZnS Quantum Dots** — ●ROBERT SCHMIDT, CORNELIUS KRASSELT, and CHRISTIAN VON BORCZYKOWSKI — Institute of Physics and nanoMA (Center for nanostructured Materials and Analytics), Chemnitz University of Technology, 09107 Chemnitz, Germany

The photoluminescence of single emitters like semiconductor quantum dots (QDs) shows intermittency, called blinking, which divides the intensity time traces into bright "on"-, dark "off"- and "gray" intermediate states, where the distribution of on- and off-times follow a power-law [1]. While these states can be well described by a charge separation model, the physical background of the blinking dynamics, especially

of the “on”-states, is less evident. Here we investigate the fluorescence of single CdSe/ZnS-QD by single photon counting techniques and use the “change-point analysis” [2] to analyze their fluorescence time traces with respect to photoluminescence intensities. This allows us to gain new information about the “on”-state-dynamics and further insights into the fundamental physical background of QD blinking.

[1] F. Cichos, C. von Borczyskowski & M. Orrit, *Current Opinion in Colloid & Interface Science* **12**, 272-284 (2007).

[2] L.P. Watkins & H. Yang, *J. Phys. Chem. B* **109**, 617-628 (2005).

CPP 48.7 Fri 12:00 ZEU 114

**Truly two-dimensional colloidal nanocrystals** — ●CHRISTIAN KLINKE — Institute of Physical Chemistry, University of Hamburg

Controlled assembly leading to anisotropic nanostructures poses a conceptual challenge in materials research. Oriented attachment of nanocrystal, a self-assembly of particles into larger single crystalline objects, is one of the most promising approaches in nanotechnology to synthesize anisotropic materials. One-dimensional assemblies of oriented attachment have been reported, and in most cases the anisotropy during self-assembly is caused by crystal planes with preferred reactivity and dipole moments in the crystallites. Systems with cubic crystal symmetry, however, like PbS and PbSe, where beautiful one-dimensional oriented attachment occurs, are somewhat more difficult to explain. In a new approach we synthesized truly two-dimensional nanocrystals by oriented attachment with lateral dimensions on the micrometer scale. We show that the formation of ordered and densely packed ligand surface layers of oleic acid on {100} PbS surfaces can drive the normally isotropic crystal growth into a two-dimensional oriented attachment of nanocrystals. Hereby the presence of chlorine containing co-solvents during the initial nucleation and growth process of the nanocrystals plays a prominent role. In the talk the synthesis and the formation mechanism will be discussed and detailed characterizations will be introduced. The obtained two-dimensional structures can be readily integrated in a photo-detector device without further treatment.

Literature: Schliehe et al., *Science* **329** (2010) 550.

CPP 48.8 Fri 12:15 ZEU 114

**XAS and XMCD Studies on Novel Iron Oxide Nanoparticles as Magnetic Resonance Imaging (MRI) Contrast Enhancers** — ●PATRICK STUMPF<sup>1</sup>, CHRISTINA GRAF<sup>1</sup>, DETLEF SCHMITZ<sup>2</sup>, CHRISTIAN GORONCY<sup>1</sup>, MARIE KÜSSNER<sup>1</sup>, and ECKART RÜHL<sup>1</sup> — <sup>1</sup>Institut für Chemie und Biochemie - Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustr. 3, D-14195 Berlin — <sup>2</sup>Helmholtz-Zentrum Berlin, Albert-Einstein-Str. 15, D-12489 Berlin

Iron oxide (FeOx) nanoparticles are applied in medical research as contrast agents in magnetic resonance imaging (MRI) where they reduce the spin-spin relaxation time (T2 time) of absorbing tissue. Their magnetic properties strongly depend on the particle size and shape, as well as the surface structure and the modification of the iron oxide core. Therefore, monodisperse, spherical iron oxide (Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub>) nanoparticles were prepared by a high temperature approach using iron oleate precursors prepared in oxygen-free and oxygen-rich surrounding. These freshly synthesized particles are tempered in an oxygen-free or oxygen-rich environment to improve their crystalline order and to change their magnetite-to-maghemite ratio. Magnetic relaxometry measurements are carried out to evaluate if these structural changes influence the spin-spin (T2) and spin-lattice (T1) relaxation times of the nanoparticles. NEXAFS (Near Edge X-Ray Absorption Fine Struc-

ture) and XMCD (X-Ray Magnetic Circular Dichroism) experiments were used to investigate local structural and electronic properties of the iron oxide particles before and after post-synthetic oxidative and thermal treatment. These results are correlated with relaxometry data.

CPP 48.9 Fri 12:30 ZEU 114

**Synthesis, characterization, and surface functionalization of gadolinium-based nanoparticles as fluorescent and magnetic probes** — ●SHIH-HAO KUNG<sup>1</sup>, CHRISTINA GRAF<sup>1</sup>, CHRISTINE BOEGLIN<sup>2</sup>, and ECKART RÜHL<sup>1</sup> — <sup>1</sup>Institut für Chemie und Biochemie, Takustr. 3, Freie Universität Berlin, 14195 Berlin, Germany — <sup>2</sup>Institute de Physique et Chimie des Matériaux de Strasbourg, 23, rue du Loess, BP43, F-67034 Strasbourg, France

The aim of this work is the investigation of nanoparticles which can be applied as combined fluorescent labels and T<sub>1</sub>-weighted magnetic resonance imaging (MRI) contrast agents. Gd<sup>3+</sup> with its seven unpaired electrons provides the magnetic contrast. Doping the nanoparticles with other rare earth elements, such as europium or erbium, makes the particles fluorescent. The present work is divided into two parts. The first part is a study on the magnetic properties of Gd<sup>3+</sup> in the particles as well as changes when the particles are doped with fluorescent Eu<sup>3+</sup>. This is achieved by X-ray magnetic circular dichroism (XMCD) measurements which were carried out at the Swiss Light Source. In the second part, results on the functionalization of nanoparticles which contain Gd<sup>3+</sup> and Er<sup>3+</sup> with biocompatible, hydrophilic ligands are presented. Mono- and bivalent polyethylene oxide-phosphonate ligands are prepared and the bond between the ligands and the particles are investigated by infrared spectroscopy. The ligand density is estimated by thermal gravimetric analysis. Moreover, the stability of the ligand-exchanged particles is studied by transmission electron microscopy and dynamic light scattering.

CPP 48.10 Fri 12:45 ZEU 114

**Effective rate constants for nanostructured heterogeneous catalysts** — ●SHAUN HENDY<sup>1,2</sup>, NAT LUND<sup>2</sup>, and NICOLA GASTON<sup>1,2</sup> — <sup>1</sup>Industrial Research Ltd, Lower Hutt 5010, New Zealand — <sup>2</sup>MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington 6140, New Zealand

There is currently a high level of interest in the use of nanoparticles for catalysis. With precious metal catalysts such as platinum and palladium in high demand, the use of these materials in nanoparticle form can also substantially reduce the cost of the catalyst through the exposure of more surface area for the same volume of material. When reactants are plentiful, the effective activity of a nanoparticulate catalyst will increase with its surface area, assuming that its shape is held constant and ignoring the effect of corners and edges. However, under diffusion-limited conditions, high surface area and a high density of active sites may bring diminishing returns as sites consume reactant faster than it arrives. Here we apply a mathematical homogenisation approach to derive simple expressions for the effective reactivity of a nanostructured catalyst under diffusion limited conditions that relate the intrinsic rate constants of the surfaces presented by the catalyst to an effective rate constant. When highly active catalytic sites, such as step edges or other defects are present, we show that distinct limiting cases emerge depending on the degree of overlap of the reactant depletion zone about each site. We discuss implications for the optimal design of nanoparticle catalysts.